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Henry F. Schaefer III

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Georgia Univ Research Foundation Inc
Boyd Grad Studies Res Cntr
Athens, GA 30602

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AFOSR/NC NL
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20332-6448
Dr Berman

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13. ABSTRACT *(Maximum 200 words)*

The object of this research is to characterize, using ab initio quantum mechanical methods, the stabilizing or destablizing effects of hydrogen and/or oxygen matrices on proposed high energy density molecular (HEDM) systems. In addition, the unimolecular fragmentation reactions of large HEDM species such as N_{20} will be studied via density functional methods.

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"Environmental Effects on High Energy Density Materials"

Principal Investigator: Henry F. Schaefer III

Center for Computational Quantum Chemistry

University of Georgia

I. Summary

The development of efficient and safe conventional (i.e., nonnuclear) propellants and/or fuels is a goal of obvious technological significance. A desirable quality of such a propellant is clearly a high ratio of energy release to mass. The present hypothesis rests on a simple, but previously unrecognized, analogy between oxygen and sulfur. Preliminary studies showed that the oxygen ring systems are sufficiently promising to warrant the detailed, high-level theoretical research reported here.

Our idea begins with the observation that elemental sulfur exists as sulfur rings, S_n. The essence of our proposal is to make an analogy between sulfur rings and oxygen rings. Given the remarkable stability of sulfur rings, should it not be possible to prepare oxygen rings? Oxygen lies directly above sulfur in the Periodic Table, and the analogy is an appealing one.

Work completed during the past year (to September 1, 1994) concerns the prospective HEDM material $C_2H_2Li_2$. This molecule has been of sustained intellectual interest since 1976 when Paul Schleyer and John Pople suggested that the lowest triplet state of 1,1 -diliythioethylene might allow nearly free rotation about the supposed classical

C=C "double bond". In 1985 Manceron and Andrews intercepted dilithioethylene via matrix isolation infrared spectroscopy in the laboratory. Moreover, in 1987 Maercker, Graule, and Demuth used mercury precursors to characterize *cis* and *trans* 1,2-dilithioethylene as more conventional reaction products. So this species is by no means simply a figment of the theorist's imagination.

The work I describe was recently accepted for publication in the *Journal of the American Chemical Society*, having been carried out jointly with the Proctor and Gamble Company. The bulk of the research was carried out by my fourth year graduate student Evan Bolton, supported by the AASERT program.

The potential energy surface (PES) for the singlet 1,2-dilithioethene and acetylenic $C_2H_2Li_2$ isomers was carefully surveyed using high level quantum mechanical methods. Three previously undiscovered minima (including, remarkably, the global minimum) were located: a planar monobridged *trans* 1,2 dilithioethene and two acetylenic structures. A total of seven minima and ten transition states for interconversion of minima were investigated, while seven transition states are located for the first time. Vibrational frequencies were evaluated for all structures through the coupled-cluster method including all single and double excitation with a double-ζ plus polarization basis set. A remarkable isomer, the C_s complex between lithioacetylene and LiH, is the global minimum on the $C_2H_2Li_2$ PES. This structure was 34 kcal/mol more stable than the two lowest lying singlet 1,2-dilithioethene structures, a *trans* planar C_{2h} form with acute CCLi angles and a *cis* doubly bridged C_{2v} structure . The other singlet 1,2-dilithioethene minima , *cis* planar monobridged C_s, *cis* planar dibridged C_{2v} , and *trans* planar monobridged C_s, are 4.3, 8.4, and 19.4 kcal/mol higher lying, respectively. The carbon-lithium bonding is ionic in character in all these species.

II. Publications (Since September 1, 1993)

1. E. E. Bolton, H. F. Schaefer, W. D. Laidig, and P. R. Schleyer, "Singlet $C_2H_2Li_2$: Acetylenic and 1, 2 - Dilithioethene Isomers. A Remarkably Congested Potential Energy Hypersurface for a Simple Organometallic System", *J. Amer. Chem. Soc.*, to appear in 1994.

III. List of Participating Professionals

A. Senior Research Personnel:

Professor Henry F. Schaefer III

B. Junior Research Personnel:

Mr. Evan E. Bolton